PATENT COOPERATION TREATY

PCT

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

(Chapter II of the Patent Cooperation Treaty)

(PCT Article 36 and Rule 70)

REC'D 21 AUG 2007
WIPO PCT

Applicant's or agent's file reference 421/90 PCT	FOR FURTHER ACTION	See Form PCT/IPEA/416
International application No. PCT/US04/42706	International filing date *(day/month/year)* 20 December 2004 (20.12.2004)	Priority date *(day/month/year)* 19 December 2003 (19.12.2003)
International Patent Classification (IPC) or national classification and IPC IPC: **H01L 21/302**(2006.01) USPC: 438/738		
Applicant THE UNIVERSITY OF NORTH CAROLINA AT CHAPEL HILL		

1. This report is the international preliminary examination report, established by this International Preliminary Examining Authority under Article 35 and transmitted to the applicant according to Article 36.
2. This REPORT consists of a total of 3 sheets, including this cover sheet.
3. This report is also accompanied by ANNEXES, comprising:

   a. ☒ *(sent to the applicant and to the International Bureau)* a total of 22 sheets, as follows:

   ☐ sheets of the description, claims and/or drawings which have been amended and are the basis of this report and/or sheets containing rectifications authorized by this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions).

   ☐ sheets which supersede earlier sheets, but which this Authority considers contain an amendment that goes beyond the disclosure in the international application as filed, as indicated in item 4 of Box No. I and the Supplemental Box.

   b. ☐ *(sent to the International Bureau only)* a total of (indicate type and number of electronic carrier(s)) _____ , containing a sequence listing and/or tables related thereto, in electronic form only, as indicated in the Supplemental Box Relating to Sequence Listing (see Section 802 of the Administrative Instructions).

4. This report contains indications relating to the following items:

☒	Box No. I	Basis of the report
☐	Box No. II	Priority
☐	Box No. III	Non-establishment of opinion with regard to novelty, inventive step and industrial applicability
☐	Box No. IV	Lack of unity of invention
☒	Box No. V	Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement
☐	Box No. VI	Certain documents cited
☐	Box No. VII	Certain defects in the international application
☐	Box No. VIII	Certain observations on the international application

Date of submission of the demand	Date of completion of this report
26 May 2005 (26.05.2005)	09 July 2007 (09.07.2007)
Name and mailing address of the IPEA/ US Mail Stop PCT, Attn: IPEA/US Commissioner for Patents P.O. Box 1450 Alexandria, Virginia 22313-1450 Facsimile No. (571) 273-3201	Authorized officer Manuel Mendez /. Hurley for Telephone No. 571-272-3700

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US04/42706

Box No. I Basis of the report

1. With regard to the **language**, this report is based on:
   - [x] the international application in the language in which it was filed.
   - [ ] a translation of the international application into ______, which is the language of a translation furnished for the purposes of:
     - [ ] international search (under Rules 12.3 and 23.1(b))
     - [ ] publication of the international application (under Rule 12.4(a))
     - [ ] international preliminary examination (under Rules 55.2(a) and/or 55.3(a))

2. With regard to the **elements** of the international application, this report is based on *(replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report)*:
   - [ ] the international application as originally filed/furnished
   - [x] the description:
     pages 1-10,12-14,17,19-21,23,25-31,34-37,40,42-43,48-83 and 85-104 as originally filed/furnished
     pages* 11,15-16,18,22,24,32-33,38-39,41,44-47 and 84 received by this Authority on 26 May 2005 (26.05.2005)
     pages* NONE received by this Authority on ______
   - [x] the claims:
     pages 105,107-112,114,117 and 119-122 as originally filed/furnished
     pages* NONE as amended (together with any statement) under Article 19
     pages* 106,113,115-116 and 118 received by this Authority on 26 May 2005 (26.05.2005)
     pages* NONE received by this Authority on ______
   - [x] the drawings:
     pages 1-7 and 9-31 as originally filed/furnished
     pages* 8 received by this Authority on 26 May 2005 (26.05.2005)
     pages* NONE received by this Authority on ______
   - [ ] a sequence listing and/or any related table(s) - see Supplemental Box Relating to Sequence Listing.

3. [ ] The amendments have resulted in the cancellation of:
   - [ ] the description, pages ______
   - [ ] the claims, Nos. ______
   - [ ] the drawings, sheets/figs ______
   - [ ] the sequence listing (*specify*): ______
   - [ ] any table(s) related to the sequence listing (*specify*): ______

4. [ ] This report has been established as if (some of) the amendments annexed to this report and listed below had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).
   - [ ] the description, pages ______
   - [ ] the claims, Nos. ______
   - [ ] the drawings, sheets/figs ______
   - [ ] the sequence listing (*specify*): ______
   - [ ] any table(s) related to the sequence listing (*specify*): ______

* *If item 4 applies, some or all of those sheets may be marked "superseded."*

INTERNATIONAL PRELIMINARY REPORT ON PATENTABILITY

International application No.
PCT/US04/42706

Box No. V Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement

1. Statement

Novelty (N)	Claims 1-135	YES
	Claims NONE	NO
Inventive Step (IS)	Claims 1-135	YES
	Claims NONE	NO
Industrial Applicability (IA)	Claims 1-135	YES
	Claims NONE	NO

2. Citations and Explanations (Rule 70.7)

Claims 1-135 meet the criteria set out in PCT Article 33(2)-(3), because the prior art does not teach or fairly suggest, *inter alia*, a method for forming one or more particles comprising the steps of providing a patterned template and a substrate disposing a volume of liquid material in or on at least one of the patterned template surface, and the plurality of recessed areas, and forming one or more particles by one of contacting the patterned template surface with the substrate and treating the liquid material.

Claims 1-135 meet the criteria set out in PCT Article 33(4), and thus have industrial applicability because the subject matter claimed can be made or used in industry.

proceeds when taken in connection with the accompanying Drawings and Examples as best described herein below.

BRIEF DESCRIPTION OF THE DRAWINGS

Figures 1A-1D are a schematic representation of an embodiment of the presently disclosed method for preparing a patterned template.

Figures 2A-2F are a schematic representation of the presently disclosed method for forming one or more micro- and/or nanoscale particles.

Figures 3A-3F are a schematic representation of the presently disclosed method for preparing one or more spherical particles.

Figures 4A-4D are a schematic representation of the presently disclosed method for fabricating charged polymeric particles. Fig. 4A represents the electrostatic charging of the molded particle during polymerization or crystallization; Fig. 4B represents a charged nano-disc; Fig. 4C represents typical random juxtapositioning of uncharged nano-discs; and Fig. 4D represents the spontaneous aggregation of charged nano-discs into chain-like structures.

Figures 5A-5C are a schematic illustration of multilayer particles that can be formed using the presently disclosed soft lithography method.

Figures 6A-6C are a schematic representation of the presently disclosed method for making three-dimensional nanostructures using a soft lithography technique.

Figures 7A-7F are a schematic representation of an embodiment of the presently disclosed method for preparing a multi-dimensional complex structure.

Figures 8A-8E are a schematic representation of the presently disclosed imprint lithography process resulting in a “scum layer.”

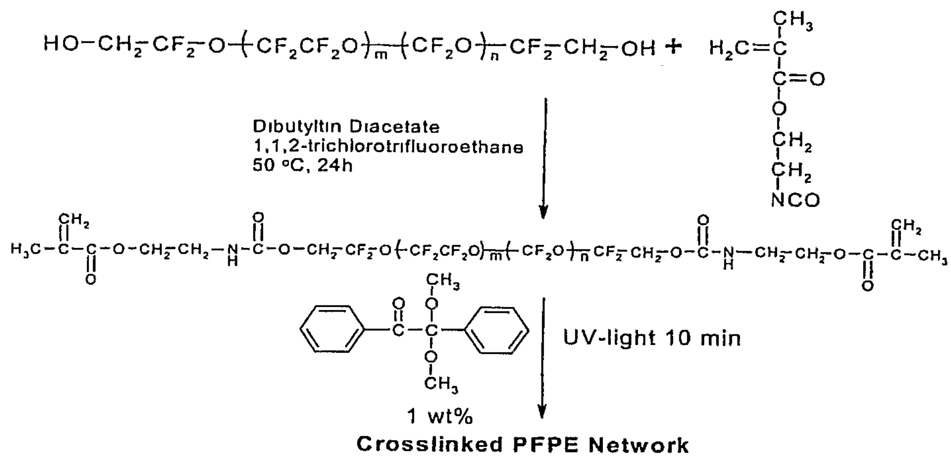
Figures 9A-9E are a schematic representation of the presently disclosed imprint lithography method, which eliminates the “scum layer” by using a functionalized, non-wetting patterned template and a non-wetting substrate.

comprises a solvent resistant, elastomer-based material, such as but not limited to a fluorinated elastomer-based material.

Further, the presently disclosed subject matter describes the first nano-contact molding of organic materials to generate high fidelity features using an elastomeric mold. Accordingly, the presently disclosed subject matter describes a method for producing free-standing, isolated micro- and nanostructures of any shape using soft or imprint lithography techniques. Representative micro- and nanostructures include but are not limited to micro- and nanoparticles, and micro- and nano-patterned substrates.

The nanostructures described by the presently disclosed subject matter can be used in several applications, including, but not limited to, semiconductor manufacturing, such as molding etch barriers without scum layers for the fabrication of semiconductor devices; crystals; materials for displays; photovoltaics; a solar cell device; optoelectronic devices; routers; gratings; radio frequency identification (RFID) devices; catalysts; fillers and additives; detoxifying agents; etch barriers; atomic force microscope (AFM) tips; parts for nano-machines; the delivery of a therapeutic agent, such as a drug or genetic material; cosmetics; chemical mechanical planarization (CMP) particles; and porous particles and shapes of any kind that will enable the nanotechnology industry.

Representative solvent resistant elastomer-based materials include but are not limited to fluorinated elastomer-based materials. As used herein, the term “solvent resistant” refers to a material, such as an elastomeric material that neither swells nor dissolves in common hydrocarbon-based organic solvents or acidic or basic aqueous solutions. Representative fluorinated elastomer-based materials include but are not limited to perfluoropolyether (PFPE)-based materials. A photocurable liquid PFPE exhibits desirable properties for soft lithography. A representative scheme for the synthesis and photocuring of functional PFPEs is provided in Scheme 1.



Scheme 1. Synthesis and Photocuring of Functional Perfluoropolyethers.

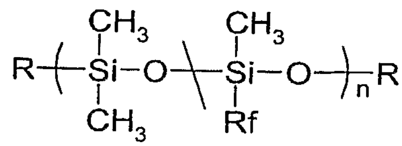
Additional schemes for the synthesis of functional perfluoropolyethers are provided in Examples 7.1 through 7.6.

This PFPE material has a low surface energy (for example, about 12 mN/m); is non-toxic, UV transparent, and highly gas permeable; and cures into a tough, durable, highly fluorinated elastomer with excellent release properties and resistance to swelling. The properties of these materials can be tuned over a wide range through the judicious choice of additives, fillers, reactive co-monomers, and functionalization agents. Such properties that are desirable to modify, include, but are not limited to, modulus, tear strength, surface energy, permeability, functionality, mode of cure, solubility and swelling characteristics, and the like. The non-swelling nature and easy release properties of the presently disclosed PFPE materials allows for nanostructures to be fabricated from any material. Further, the presently disclosed subject matter can be expanded to large scale rollers or conveyor belt technology or rapid stamping that allow for the fabrication of nanostructures on an industrial scale.

In some embodiments, the patterned template comprises a solvent resistant, low surface energy polymeric material derived from casting low viscosity liquid materials onto a master template and then curing the low

In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

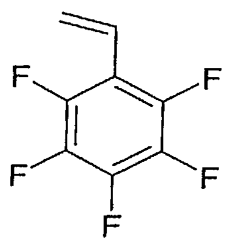
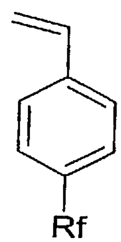


wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

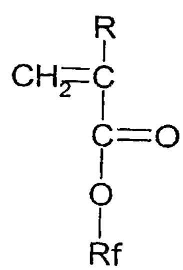
Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:


and

,

wherein Rf comprises a fluoroalkyl chain.

In some embodiments, the acrylate material comprises a fluorinated acrylate or a fluorinated methacrylate having the following structure:



wherein:

R is selected from the group consisting of H, alkyl, substituted alkyl, aryl, and substituted aryl; and

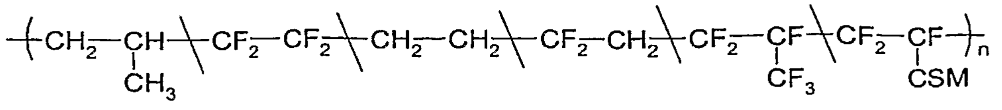
are produced in a continuous process is schematically presented. An apparatus **199** is provided for carrying out the process. Indeed, while Figure 2F schematically presents a continuous process for particles, apparatus **199** can be adapted for batch processes, and for providing a pattern on a substrate continuously or in batch, in accordance with the presently disclosed subject matter and based on a review of the presently disclosed subject matter by one of ordinary skill in the art.

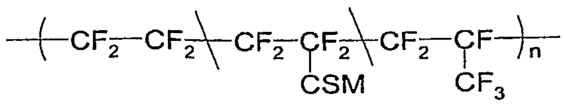
Continuing, then, with Figure 2F, droplet **204** of liquid material is applied to substrate **200'** via reservoir **203**. Substrate **200'** can be coated or not coated with a non-wetting agent. Substrate **200'** and pattern template **108'** are placed in a spaced relationship with respect to each other and are also operably disposed with respect to each other to provide for the conveyance of droplet **204** between patterned template **108'** and substrate **200'**. Conveyance is facilitated through the provision of pulleys **208**, which are in operative communication with controller **201**. By way of representative non-limiting examples, controller **201** can comprise a computing system, appropriate software, a power source, a radiation source, and/or other suitable devices for controlling the functions of apparatus **199**. Thus, controller **201** provides for power for and other control of the operation of pulleys **208** to provide for the conveyance of droplet **204** between patterned template **108'** and substrate **200'**. Particles **206** are formed and treated between substrate **200'** and patterned template **108'** by a treating process $\mathbf{T_R}$, which is also controlled by controller **201**. Particles **206** are collected in an inspecting device **210**, which is also controlled by controller **201**. Inspecting device **210** provides for one of inspecting, measuring, and both inspecting and measuring one or more characteristics of particles **206**. Representative examples of inspecting devices **210** are disclosed elsewhere herein.

Thus, in some embodiments, the method for forming one or more particles comprises:

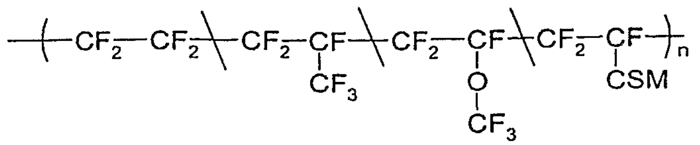
(a) providing a patterned template and a substrate, wherein the patterned template comprises a first patterned template surface having a plurality of recessed areas formed therein;

(b) disposing a volume of liquid material in or on at least one of:





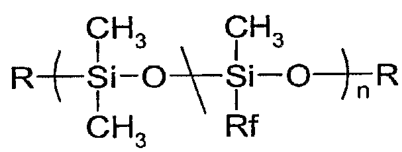
, and



wherein CSM comprises a cure site monomer.

In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

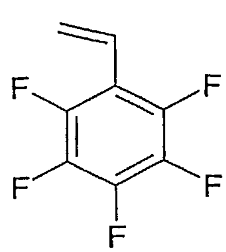


wherein:

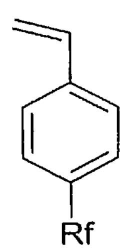
R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:



and



,

wherein Rf comprises a fluoroalkyl chain.

embodiments, the method comprises designing the particles to include a specific biological recognition motif. In some embodiments, the biological recognition motif comprises biotin/avidin and/or other proteins.

In some embodiments, the method comprises tailoring the chemical composition of these materials and controlling the reaction conditions, whereby it is then possible to organize the biorecognition motifs so that the efficacy of the particle is optimized. In some embodiments, the particles are designed and synthesized so that recognition elements are located on the surface of the particle in such a way to be accessible to cellular binding sites, wherein the core of the particle is preserved to contain bioactive agents, such as therapeutic molecules. In some embodiments, a non-wetting imprint lithography method is used to fabricate the objects, wherein the objects are optimized for a particular application by incorporating functional motifs, such as biorecognition agents, into the object composition. In some embodiments, the method further comprises controlling the microscale and nanoscale structure of the object by using methods selected from the group consisting of self-assembly, stepwise fabrication procedures, reaction conditions, chemical composition, crosslinking, branching, hydrogen bonding, ionic interactions, covalent interactions, and the like. In some embodiments, the method further comprises controlling the microscale and nanoscale structure of the object by incorporating chemically organized precursors into the object. In some embodiments, the chemically organized precursors are selected from the group consisting of block copolymers and core-shell structures.

In sum, the presently disclosed subject matter describes a non-wetting imprint lithography technique that is scalable and offers a simple, direct route to such particles without the use of self-assembled, difficult to fabricate block copolymers and other systems.

III. Formation of Rounded Particles Through "Liquid Reduction"

Referring now to Figures 3A through 3F, the presently disclosed subject matter provides a "liquid reduction" process for forming particles that have shapes that are not conformal to the shape of the template, including but not limited to spherical micro- and nanoparticles. For example, a "cube-

shaped" template can allow for sphereical particles to be made, whereas a "Block arrow-shaped" template can allow for "lolli-pop" shaped particles or objects to be made wherein the introduction of a gas allows surface tension forces to reshape the resident liquid prior to treating it. While not wishing to be bound by any particular theory, the non-wetting characteristics that can be provided in some embodiments of the presently disclosed patterned template and/or treated or coated substrate allows for the generation of rounded, e.g., spherical, particles.

Referring now to Figure 3A, droplet **302** of a liquid material is disposed on substrate **300**, which in some embodiments is coated or treated with a non-wetting material **304**. A patterned template **108**, which comprises a plurality of recessed areas **110** and patterned surface areas **112**, also is provided.

Referring now to Figure 3B, patterned template **108** is contacted with droplet **302**. The liquid material comprising droplet **302** then enters recessed areas **110** of patterned template **108**. In some embodiments, a residual, or "scum," layer **RL** of the liquid material comprising droplet **302** remains between the patterned template **108** and substrate **300**.

Referring now to Figure 3C, a first force F_{a1} is applied to patterned template **108**. A contact point **CP** is formed between the patterned template **108** and the substrate and displacing residual layer **RL**. Particles **306** are formed in the recessed areas **110** of patterned template **108**.

Referring now to Figure 3D, a second force F_{a2}, wherein the force applied by F_{a2} is greater than the force applied by F_{a1}, is then applied to patterned template **108**, thereby forming smaller liquid particles **308** inside recessed areas **112** and forcing a portion of the liquid material comprising droplet **302** out of recessed areas **112**.

Referring now to Figure 3E, the second force F_{a2} is released, thereby returning the contact pressure to the original contact pressure applied by first force F_{a1}. In some embodiments, patterned template **108** comprises a gas permeable material, which allows a portion of space with recessed areas **112** to be filled with a gas, such as nitrogen, thereby forming a plurality of liquid

7A-7F can be carried out multiple times as desired to form intricate nanostructures.

Accordingly, in some embodiments, a method for forming multidimensional structures is provided, the method comprising:

(a) providing a particle prepared by the process described in the figures;

(b) providing a second patterned template;

(c) disposing a second liquid material in the second patterned template;

(d) contacting the second patterned template with the particle of step (a); and

(e) treating the second liquid material to form a multidimensional structure.

VII. Imprint Lithography

Referring now to Figures 8A-8D, a method for forming a pattern on a substrate is illustrated. In the embodiment illustrated in Figure 8, an imprint lithography technique is used to form a pattern on a substrate.

Referring now to Figure 8A, a patterned template **810** is provided. In some embodiments, patterned template **810** comprises a solvent resistant, low surface energy polymeric material, derived from casting low viscosity liquid materials onto a master template and then curing the low viscosity liquid materials to generate a patterned template as defined hereinabove. Patterned template **810** further comprises a first patterned template surface **812** and a second template surface **814**. The first patterned template surface **812** further comprises a plurality of recesses **816**. The patterned template derived from a solvent resistant, low surface energy polymeric material could be mounted on another material to facilitate alignment of the patterned template or to facilitate continuous processing such as a conveyor belt. This might be particularly useful in the fabrication of precisely placed structures on a surface, such as in the fabrication of a complex devices or a semiconductor, electronic or photonic devices.

Referring again to Figure 8A, a substrate **820** is provided. Substrate **820** comprises a substrate surface **822**. In some embodiments, substrate **820** is selected from the group consisting of a polymer material, an inorganic material, a silicon material, a quartz material, a glass material, and surface treated variants thereof. In some embodiments, at least one of patterned template **810** and substrate **820** has a surface energy lower than 18 mN/m. In some embodiments, at least one of patterned template **810** and substrate **820** has a surface energy lower than 15 mN/m.

In some embodiments, as illustrated in Figure 8A, patterned template **810** and substrate **820** are positioned in a spaced relationship to each other such that first patterned template surface **812** faces substrate surface **822** and a gap **830** is created between first patterned template surface **812** and substrate surface **822**. This is an example of a predetermined relationship.

Referring now to Figure 8B, a volume of liquid material **840** is disposed in the gap **830** between first patterned template surface **812** and substrate surface **822**. In some embodiments, the volume of liquid material **840** is disposed directed on a non-wetting agent (not shown), which is disposed on first patterned template surface **812**.

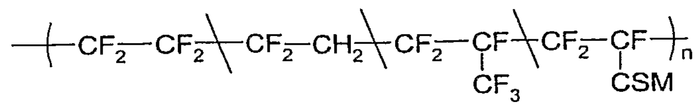
Referring now to Figure 8C, in some embodiments, first patterned template **812** is contacted with the volume of liquid material **840**. A force $\mathbf{F_a}$ is applied to second template surface **814** thereby forcing the volume of liquid material **840** into the plurality of recesses **816**. In some embodiments, as illustrated in Figure 8C, a portion of the volume of liquid material **840** remains between first patterned template surface **812** and substrate surface **820** after force $\mathbf{F_a}$ is applied.

Referring again to Figure 8C, in some embodiments, the volume of liquid material **840** is treated by a treating process $\mathbf{T_r}$ while force $\mathbf{F_a}$ is being applied to form a treated liquid material **842**. In some embodiments, treating process $\mathbf{T_r}$ comprises a process selected from the group consisting of a thermal process, a photochemical process, and a chemical process.

Referring now to Figure 8D, a force $\mathbf{F_r}$ is applied to patterned template **810** to remove patterned template **810** from treated liquid material **842** to reveal a pattern **850** on substrate **820** as shown in Figure 8E. In some

wherein X is present or absent, and when present comprises an endcapping group.

In some embodiments, the fluoroolefin material is selected from the group consisting of:



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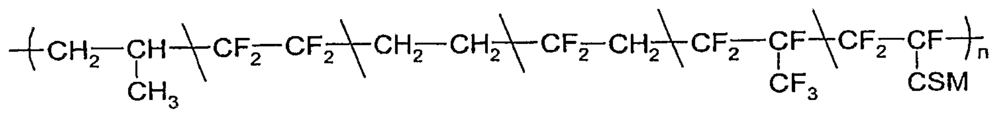

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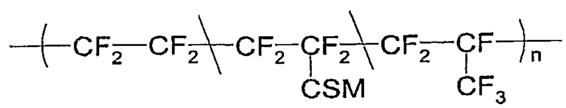
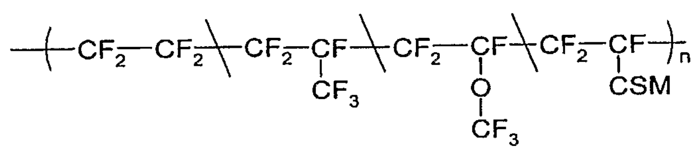


, and



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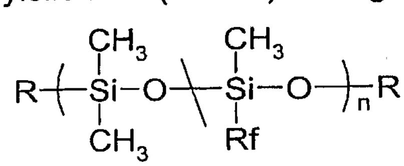
wherein CSM comprises a cure site monomer.

In some embodiments, the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

In some embodiments, the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:



wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

In some embodiments, the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:

In some embodiments, the disposing of the volume of liquid material is regulated by a spreading process. In some embodiments, the spreading process comprises:

(a) disposing a first volume of liquid material on the patterned template to form a layer of liquid material on the patterned template; and

(b) drawing an implement across the layer of liquid material to:

   (i) remove a second volume of liquid material from the layer of liquid material on the patterned template; and

   (ii) leave a third volume of liquid material on the patterned template.

In some embodiments, the contacting of the first template surface with the substrate eliminates essentially all of the disposed volume of liquid material.

In some embodiments, the treating of the liquid material comprises a process selected from the group consisting of a thermal process, a photochemical process, and a chemical process.

In some embodiments, the method comprises a batch process. In some embodiments, the batch process is selected from one of a semi-batch process and a continuous batch process.

In some embodiments, the presently disclosed subject matter describes a patterned substrate formed by the presently disclosed methods.

VIII. Imprint Lithography Free of a Residual "Scum Layer"

A characteristic of imprint lithography that has restrained its full potential is the formation of a "scum layer" once the liquid material, e.g., a resin, is patterned. The "scum layer" comprises residual liquid material that remains between the stamp and the substrate. In some embodiments, the presently disclosed subject matter provides a process for generating patterns essentially free of a scum layer.

Referring now to Figures 9A-9E, in some embodiments, a method for forming a pattern on a substrate is provided, wherein the pattern is essentially free of a scum layer. Referring now to Figure 9A, a patterned template **910** is provided. Patterned template **910** further comprises a first patterned template

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surface **912** and a second template surface **914**. The first patterned template surface **912** further comprises a plurality of recesses **916**. In some embodiments, a non-wetting agent **960** is disposed on the first patterned template surface **912**.

Referring again to Figure 9A, a substrate **920** is provided. Substrate **920** comprises a substrate surface **922**. In some embodiments, a non-wetting agent **960** is disposed on substrate surface **920**.

In some embodiments, as illustrated in Figure 9A, patterned template **910** and substrate **920** are positioned in a spaced relationship to each other such that first patterned template surface **912** faces substrate surface **922** and a gap **930** is created between first patterned template surface **912** and substrate surface **922**.

Referring now to Figure 9B, a volume of liquid material **940** is disposed in the gap **930** between first patterned template surface **912** and substrate surface **922**. In some embodiments, the volume of liquid material **940** is disposed directly on first patterned template surface **912**. In some embodiments, the volume of liquid material **940** is disposed directly on non-wetting agent **960**, which is disposed on first patterned template surface **912**. In some embodiments, the volume of liquid material **940** is disposed directly on substrate surface **920**. In some embodiments, the volume of liquid material **940** is disposed directly on non-wetting agent **960**, which is disposed on substrate surface **920**.

Referring now to Figure 9C, in some embodiments, first patterned template surface **912** is contacted with the volume of liquid material **940**. A force F_a is applied to second template surface **914** thereby forcing the volume of liquid material **940** into the plurality of recesses **916**. In contrast with the embodiment illustrated in Figure 8, a portion of the volume of liquid material **940** is forced out of gap **930** by force F_o when force F_a is applied.

Referring again to Figure 9C, in some embodiments, the volume of liquid material **940** is treated by a treating process T_r while force F_a is being applied to form a treated liquid material **942**.

Referring now to Figure 9D, a force F_r is applied to patterned template **910** to remove patterned template **910** from treated liquid material **942** to reveal a pattern **950** on substrate **920** as shown in Figure 9E. In this embodiment, substrate **920** is essentially free of a residual, or "scum," layer of treated liquid material **942**.

In some embodiments, at least one of the template surface and substrate comprises a functionalized surface element. In some embodiments, the functionalized surface element is functionalized with a non-wetting material. In some embodiments, the non-wetting material comprises functional groups that bind to the liquid material. In some embodiments, the non-wetting material is selected from the group consisting of a trichloro silane, a trialkoxy silane, a trichloro silane comprising non-wetting and reactive functional groups, a trialkoxy silane comprising non-wetting and reactive functional groups, and mixtures thereof.

In some embodiments, the point of contact between the two surface elements is free of liquid material. In some embodiments, the point of contact between the two surface elements comprises residual liquid material. In some embodiments, the height of the residual liquid material is less than 30% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 20% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 10% of the height of the structure. In some embodiments, the height of the residual liquid material is less than 5% of the height of the structure. In some embodiments, the volume of liquid material is less than the volume of the patterned template. In some embodiments, substantially all of the volume of liquid material is confined to the patterned template of at least one of the surface elements. In some embodiments, having the point of contact between the two surface elements free of liquid material retards slippage between the two surface elements.

IX. Solvent-Assisted Micro-molding (SAMIM)

In some embodiments, the presently disclosed subject matter describes a solvent-assisted micro-molding (SAMIM) method for forming a pattern on a substrate.

Referring now to Figure 10A, a patterned template **1010** is provided. Patterned template **1010** further comprises a first patterned template surface **1012** and a second template surface **1014**. The first patterned template surface **1012** further comprises a plurality of recesses **1016**.

Referring again to Figure 10A, a substrate **1020** is provided. Substrate **1020** comprises a substrate surface **1022**. In some embodiments, a polymeric material **1070** is disposed on substrate surface **1022**. In some embodiments, polymeric material **1070** comprises a resist polymer.

Referring again to Figure 10A, patterned template **1010** and substrate **1020** are positioned in a spaced relationship to each other such that first patterned template surface **1012** faces substrate surface **1022** and a gap **1030** is created between first patterned template surface **1012** and substrate surface **1022**. As shown in Figure 10A, a solvent **S** is disposed within gap **1030**, such that solvent **S** contacts polymeric material **1070** forming a swollen polymeric material **1072**.

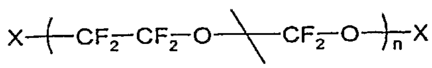
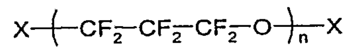
Referring now to Figures 10B and 10C, first patterned template surface **1012** is contacted with swollen polymeric material **1072**. A force $\mathbf{F_a}$ is applied to second template surface **1014** thereby forcing a portion of swollen polymeric material **1072** into the plurality of recesses **1016** and leaving a portion of swollen polymeric material **1072** between first patterned template surface **1012** and substrate surface **1020**. The swollen polymeric material **1072** is then treated by a treating process $\mathbf{T_r}$ while under pressure.

Referring now to Figure 10D, a force $\mathbf{F_r}$ is applied to patterned template **1010** to remove patterned template **1010** from treated swollen polymeric material **1072** to reveal a polymeric pattern **1074** on substrate **1020** as shown in Figure 10E.

established. By repeating this methodology with different particle formulations, many combinations of therapeutic agents, tissue targeting agents, release agents, and other important compounds can be rapidly screened to determine the optimal combination for a desired therapeutic application.

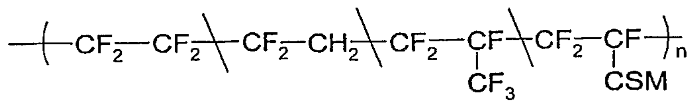
Example 3.26 Fabrication of a shape-specific PEG membrane

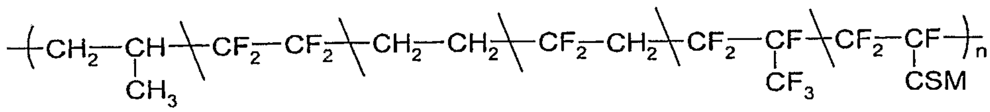
A patterned perfluoropolyether (PFPE) mold is generated by pouring a PFPE-dimethacrylate (PFPE-DMA) containing 1-hydroxycyclohexyl phenyl ketone over a silicon substrate patterned with 3-μm cylindrical holes that are 5 μm deep. A poly(dimethylsiloxane) mold is used to confine the liquid PFPE-DMA to the desired area. The apparatus is then subjected to UV light (λ = 365 nm) for 10 minutes while under a nitrogen purge. The fully cured PFPE-DMA mold is then released from the silicon master. Separately, a poly(ethylene glycol) (PEG) diacrylate (n=9) is blended with 1 wt% of a photoinitiator, 1-hydroxycyclohexyl phenyl ketone. Flat, uniform, non-wetting surfaces are generated by treating a silicon wafer cleaned with "piranha" solution (1:1 concentrated sulfuric acid:30% hydrogen peroxide (aq) solution) with trichloro(1H, 1H, 2H, 2H-perfluorooctyl) silane via vapor deposition in a desiccator for 20 minutes. Following this, 50 μL of PEG diacrylate is then placed on the treated silicon wafer and the patterned PFPE mold placed on top of it. The substrate is then placed in a molding apparatus and a small pressure is applied to push out excess PEG-diacrylate. The entire apparatus is then subjected to UV light (λ = 365 nm) for ten minutes while under a nitrogen purge. An interconnected membrane is observed after separation of the PFPE mold and the treated silicon wafer using scanning electron microscopy (SEM). The membrane is released from the surface by soaking in water and allowing it to lift off the surface.

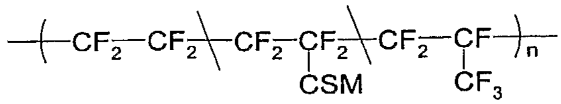
, and ;

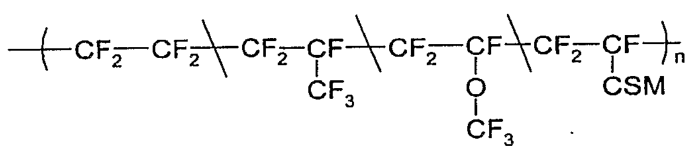
wherein X is present or absent, and when present comprises an endcapping group.

6. The method of Claim 4, wherein the fluoroolefin material is selected from the group consisting of:

,

,

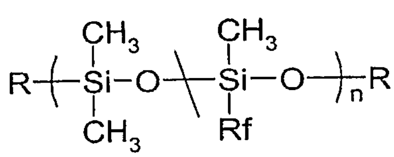
, and

,

wherein CSM comprises a cure site monomer.

7. The method of Claim 4, wherein the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride, hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

8. The method of Claim 4, wherein the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:



wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

Rf comprises a fluoroalkyl chain.

(c) delivering the particle comprising the therapeutic agent to the target.

58. The method of Claim 57, wherein the therapeutic agent is selected from one of a drug and genetic material.

59. The method of Claim 58, wherein the genetic material is selected from the group consisting of a non-viral gene vector, DNA, RNA, RNAi, and a viral particle.

60. The method of Claim 57, wherein the particle comprises a biodegradable polymer.

61. The method of Claim 60, wherein the biodegradable polymer is selected from the group consisting of a polyester, a polyanhydride, a polyamide, a phosphorous-based polymer, a poly(cyanoacrylate), a polyurethane, a polyorthoester, a polydihydropyran, and a polyacetal.

62. The method of Claim 61, wherein the polyester is selected from the group consisting of polylactic acid, polyglycolic acid, poly(hydroxybutyrate), poly(ϵ-caprolactone), poly(β-malic acid), and poly(dioxanones).

63. The method of Claim 61, wherein the polyanhydride is selected from the group consisting of poly(sebacic acid), poly(adipic acid), and poly(terpthalic acid).

64. The method of Claim 61, wherein the polyamide is selected from the group consisting of poly(imino carbonates) and polyaminoacids.

65. The method of Claim 61, wherein the phosphorous-based polymer is selected from the group consisting of a polyphosphate, a polyphosphonate, and a polyphosphazene.

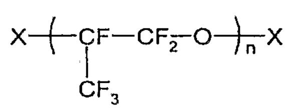
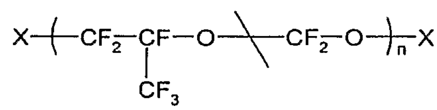
66. The method of Claim 60, wherein the biodegradable polymer further comprises a polymer that is responsive to a stimulus.

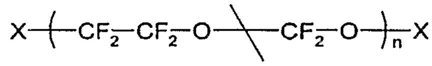
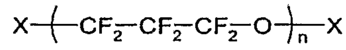
67. The method of Claim 66, wherein the stimulus is selected from the group consisting of pH, radiation, ionic strength, temperature, an alternating magnetic field, and an alternating electric field.

68. The method of Claim 67, wherein the stimulus comprises an alternating magnetic field.

78. The method of Claim 76, wherein at least one of the patterned template and substrate comprises a material selected from the group consisting of a perfluoropolyether material, a fluoroolefin material, an acrylate material, a silicone material, a styrenic material, a fluorinated thermoplastic elastomer (TPE), a triazine fluoropolymer, a perfluorocyclobutyl material, a fluorinated epoxy resin, and a fluorinated monomer or fluorinated oligomer that can be polymerized or crosslinked by a metathesis polymerization reaction.

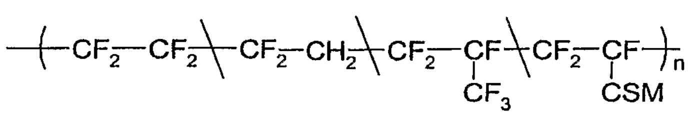
79. The method of Claim 78, wherein the perfluoropolyether material comprises a backbone structure selected from the group consisting of:

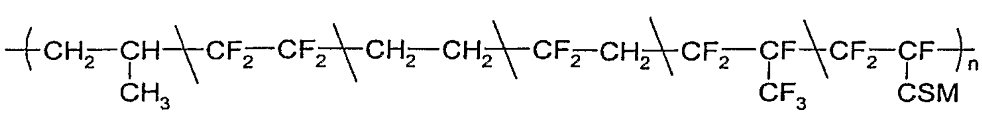
 ,  ,

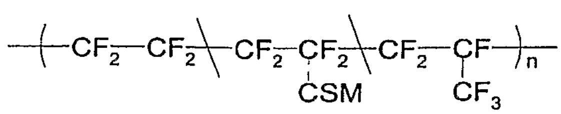
 , and  ;

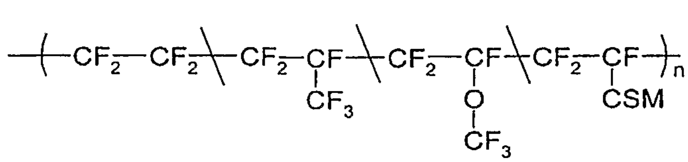
wherein X is present or absent, and when present comprises an endcapping group.

80. The method of Claim 78, wherein the fluoroolefin material is selected from the group consisting of:

 ,

 ,

 , and

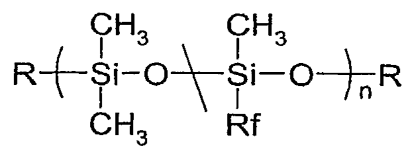
 ,

wherein CSM comprises a cure site monomer.

81. The method of Claim 78 wherein the fluoroolefin material is made from monomers which comprise tetrafluoroethylene, vinylidene fluoride,

hexafluoropropylene, 2,2-bis(trifluoromethyl)-4,5-difluoro-1,3-dioxole, a functional fluoroolefin, functional acrylic monomer, and a functional methacrylic monomer.

82. The method of Claim 78, wherein the silicone material comprises a fluoroalkyl functionalized polydimethylsiloxane (PDMS) having the following structure:

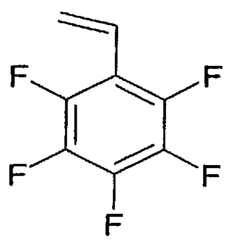
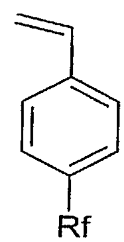


wherein:

R is selected from the group consisting of an acrylate, a methacrylate, and a vinyl group; and

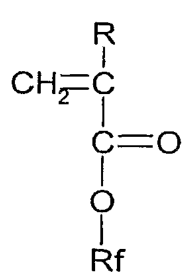
Rf comprises a fluoroalkyl chain.

83. The method of Claim 78, wherein the styrenic material comprises a fluorinated styrene monomer selected from the group consisting of:

 and  ,

wherein Rf comprises a fluoroalkyl chain.

84. The method of Claim 78, wherein the acrylate material comprises a fluorinated acrylate or a fluorinated methacrylate having the following structure:



wherein:

97. The method of Claim 94, wherein the plurality of structural features has a dimension ranging from about 1 micron to about 100 nm in size.

98. The method of Claim 94, wherein the plurality of structural features has a dimension ranging from about 100 nm to about 1 nm in size.

99. The method of Claim 76, wherein the liquid material is selected from the group consisting of a polymer, a solution, a monomer, a plurality of monomers, a polymerization initiator, a polymerization catalyst, an inorganic precursor, a metal precursor, a pharmaceutical agent, a tag, a magnetic material, a paramagnetic material, a superparamagnetic material, a ligand, a cell penetrating peptide, a porogen, a surfactant, a plurality of immiscible liquids, a solvent, and a charged species.

100. The method of Claim 99, wherein the pharmaceutical agent is selected from the group consisting of a drug, a peptide, RNAi, and DNA.

101. The method of Claim 99, wherein the tag is selected from the group consisting of a fluorescence tag, a radiolabeled tag, and a contrast agent.

102. The method of Claim 99, wherein the ligand comprises a cell targeting peptide.

103. The method of Claim 76, wherein the liquid material is selected from one of a resist polymer and a low-k dielectric.

104. The method of Claim 76, wherein the liquid material comprises a non-wetting agent.

105. The method of Claim 76, wherein the disposing of the volume of liquid material is regulated by a spreading process.

106. The method of Claim 105, wherein the spreading process comprises:

(a) disposing a first volume of liquid material on the patterned template to form a layer of liquid material on the patterned template; and

(b) drawing an implement across the layer of liquid material to:

(i) remove a second volume of liquid material from the layer of liquid material on the patterned template; and

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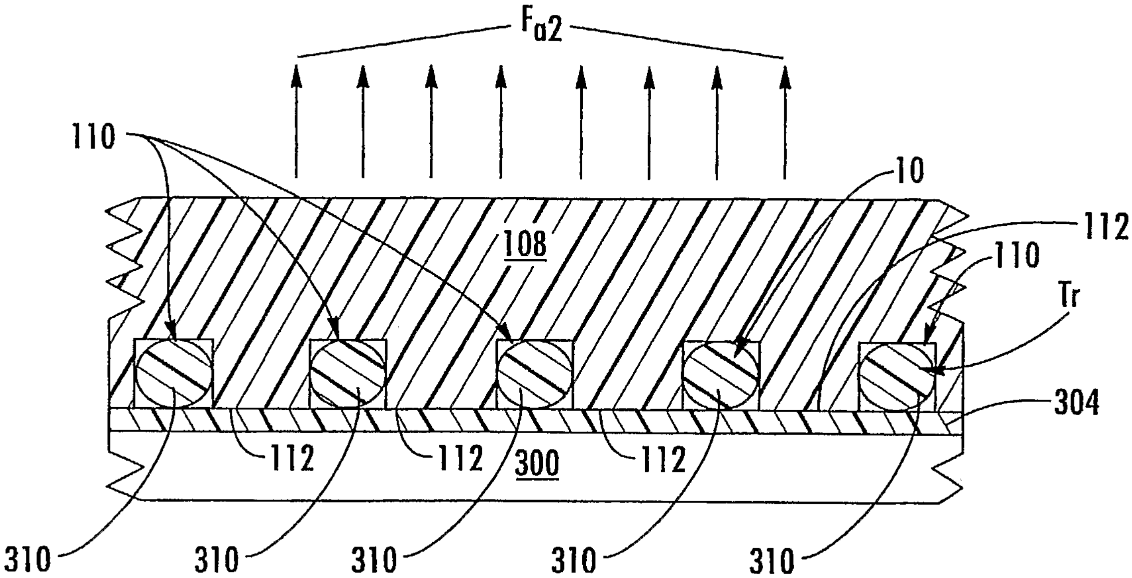
F_{a2}
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FIG. 3E

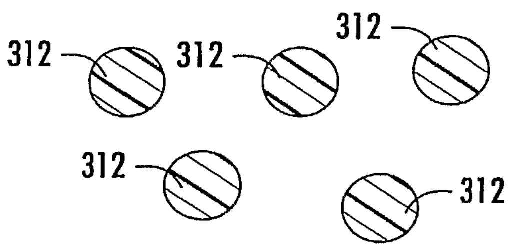
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FIG. 3F